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Exposure assessment of polycyclic aromatic hydrocarbons in refined coal tar sealant applications

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Abstract

Background—Refined coal tar sealant (RCTS) emulsions are used to seal the surface of asphalt pavement. Nine of the 22 polycyclic aromatic hydrocarbons (PAHs) evaluated in this study are classified as known, probable, or possible human carcinogens. Exposure assessment research for RCTS workers has not been published previously.

Objectives—The overall objective of this study was to develop a representative occupational exposure assessment of PAH exposure for RCTS workers based on worksite surveys. The specific aims were to: 1) quantify full-shift airborne occupational exposures to PAHs among RCTS workers; 2) quantify workers' dermal exposures to PAHs; 3) quantify biomarkers of PAH exposure in workers' urine; 4) identify specific job titles associated with RCTS exposure; and 5) apply these results to a biological exposure index to assess risk of potential genotoxicity from occupational exposures.

Methods—A total of twenty-one RCTS workers were recruited from three companies. Personal and area air samples were collected using a modification of NIOSH Method 5515. Dermal exposure was assessed by hand and neck wipes before and after shifts. Twenty-two PAHs were quantified via gas chromatography-mass spectrometry selected ion monitoring. Internal dose was estimated by quantifying select PAH metabolites in pre- and post-shift urine samples using on-line solid phase extraction-high performance liquid chromatography-tandem mass spectrometry.

Results—PAH levels in the worker breathing zones were highest for naphthalene, acenaphthene, and phenanthrene, with geometric means of 52.1, 11.4, and 9.8 μg/m^3, respectively. Hand

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

wipe levels of phenanthrene, fluoranthene and pyrene were the highest among the 22 PAHs with geometric means of 7.9, 7.7, and 5.5 μg/cm^2, respectively. Urinary PAH biomarkers for naphthalene, fluorene, phenanthrene, and pyrene were detected in all workers and were higher for post-shift samples than those collected pre-shift. Urinary concentrations of the metabolite 1-hydroxypyrene were greater than the American Conference of Governmental Industrial Hygienists (ACGIH) Biological Exposure Index (BEI) for this metabolite in 89 percent of post-shift samples collected on the final day of the work week or field survey. Statistically significances were found between concentrations of fluorene, naphthalene, and phenanthrene in the breathing zone of workers and their corresponding urinary PAH biomarkers. Workers were placed in two work place exposure groups: applicators and non-applicators. Applicators had higher total PAH concentrations in personal breathing zone (PBZ) air samples than non-applicators and were more likely to have post-shift hand wipe concentrations significantly higher than pre-shift concentrations. Concentrations of post-shift urinary biomarkers were higher, albeit not significantly, for applicators than non-applicators.

Conclusions—The exposure results from RCTS worker samples cannot be explained by proximal factors such as nearby restaurants or construction. Air and skin concentration levels were substantially higher for RCTS workers than previously published levels among asphalt workers for all PAHs. PAH profiles on skin wipes were more consistent with RCTS sealant product than air samples. Last day post-shift urinary concentrations of 1-hydroxypyrene greatly exceeded the ACGIH BEI benchmark of 2.5 μg/L in 25 of 26 samples, which suggests occupational exposure and risk of genotoxicity. When pyrene and benzo[a]pyrene were both detected, concentration ratios from personal exposure samples were used to calculate the adjusted BEI. Concentrations of 1-hydroxypyrene exceeded the adjusted BEIs for air, hand wipes, and neck wipes in most cases. These results indicate the need to increase safety controls and exposure mitigation for RCTS workers.

Keywords

Polycyclic aromatic hydrocarbons (PAHs); Coal tar sealants; N-heterocycles

1. Introduction

Coal tar pitch is a complex mixture of chemicals that includes a variety of polycyclic aromatic hydrocarbons (PAHs) and N-heterocyclic PAHs. PAHs are a class of chemicals with multiple benzene rings, while N-heterocyclic PAHs have a combination of benzene rings and N-heterocycles. Both types of PAHs are formed from incomplete combustion of organic matter, with the N-heterocycles resulting from compounds containing nitrogen. Several PAHs are classified as carcinogens, probable carcinogens, or possible carcinogens by the International Agency for Research on Cancer (IARC) (IARC, 2010, 2012). Coal tar pitch is classified as a known (Group 1) carcinogen in humans based on a combination of animal, genotoxicity, and occupational exposure studies of roofers and pavers (IARC, 2012). Research indicates that PAH carcinogenicity increases with the number of benzene rings, and therefore molecular weight (Bostrom, 2002). Tables and figures describing PAHs within this manuscript are organized by molecular weight to provide context for this carcinogenic relationship. Of the 22 PAHs addressed in this

study, one is classified as Group 1 (benzo[*a*]pyrene), one is 2A, and seven are 2B (Table 1). The United States National Toxicology Program (NTP) has listed benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, and indeno[*1,2,3-cd*]pyrene as reasonably anticipated to be human carcinogens in their Fourteenth Report on Carcinogens and has expressed interest in further research on the topic (NTP, 2016).

Coal tar pitch is the residue that remains after the distillation of crude coal tar, during which specific fractions are collected and multiple products may be produced at different temperatures and processing steps (IARC, 1985). Coal tar pitch is then separated ("refined") into fractions of 12 different viscosities. RT-12 is the most viscous and is used in manufacturing pavement sealants, as specified by American Society for Testing and Materials (ASTM) D490 (ASTM, 2016).

Refined coal tar sealant (RCTS) emulsions are applied as a protective coating for asphalt pavement. RCTS emulsions are a mixture of clay, water, sand, and RT-12. The final RCTS product applied by workers contains up to 35 percent RT-12 (McClintock et al., 2005). Some products may have other components added based on use specifications (ASTM, 2017). RCTS are predominately used east of the U.S. continental divide because they are by-products of coke production and coke plants are concentrated in the eastern part of the USA.

The United States Geological Survey (USGS) performed environmental air sampling immediately after completion of pavement seal coating with RCTS and reported elevated levels of various PAHs including some of the same chemicals listed in the occupational classification "coal tar pitch volatiles" (Van Metre et al., 2012). These findings suggest the need to evaluate occupational exposures for workers applying coal tar sealants because there is currently no published occupational exposure data for PAHs in coal tar sealant. Review of the literature found only one source of occupational airborne PAH levels from a 1984 study from New Zealand. However, the study included only two data points during coal tar spraying of a chip seal road, a process rarely used then, and no longer used in the industry (Darby et al., 1986).

The general population is exposed to PAHs through consumption of food containing PAHs, breathing ambient air, smoking cigarettes, and breathing smoke from other sources, such as vehicle exhaust (NIH, 2019). Occupational exposures generally occur as a mixture of ingestion, skin contact, and inhalation (Mumtaz and George, 1995), but more recent studies of asphalt workers found that skin and inhalation exposures are equally important contributors to occupational exposures (Cavallari et al., 2012; McClean et al., 2004; Vaananen et al., 2005).

At least three groups have developed occupational exposure limits or guidelines for seven PAHs and coal tar pitch volatiles. Naphthalene(a PAH in coal tar sealants), with two benzene rings, has the lowest molecular weight and is the most volatile PAH. Airborne naphthalene has a vacated permissible exposure limit (PEL) of 50 mg/m^3 established by the Occupational Safety and Health Administration (OSHA); a full-shift recommended exposure limit (REL) of 50 mg/m^3 as a 10-h time-weighted average (TWA) established by the National Institute of

Occupational Safety and Health (NIOSH); a NIOSH short-term exposure limit (STEL) of 75 mg/m^3 (NIOSH, 2007); and an American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) of 50 mg/m^3. Two naphthalene derivatives, 1-methylnaphthalene and 2-methylnaphthalene, each have a TLV of 3 mg/m^3 as an 8-h TWA established by the ACGIH (ACGIH, 2019). Benzo[*a*]pyrene, benzo[*b*]fluoranthene, benz[*a*]anthracene, and chrysene do not have acceptable airborne exposure levels because they have been observed to be carcinogenic in animal studies (ACGIH, 2019). Rather, the ACGIH recommends that all exposures to these compounds be reduced to levels as low as possible (ACGIH, 2019). The ACGIH has listed chrysene as a 2A carcinogen (confirmed animal carcinogen with unknown relevance in humans) and benzo[*a*]pyrene, benzo[*b*]fluoranthene, and benz[*a*]anthracene are listed as 2B carcinogens (suspected human carcinogen).

Pyrene is present in almost every PAH mixture (Hopf et al., 2009). The ACGIH developed a biological exposure index (BEI) based on the relationship between 1-hydroxypyrene and a range of genotoxicity markers, and currently recommends assessing worker exposure to PAHs by testing urine specimens for 1-hydroxypyrene, a metabolite of pyrene (ACGIH, 2019). This metabolite is considered an index chemical that acts as a surrogate marker for the absorption of various mixtures of PAHs in occupational settings. Generally, the ACGIH considers concentrations of 1-hydroxypyrene at or above 2.5 μg/L evidence of occupational exposure and risk of genotoxicity (ACGIH, 2019).

However, the ACGIH recommends calculating an adjusted Biological Exposure Index (BEI), when specific exposure information is available. The BEI is adjusted by calculating the ratio of pyrene to benzo[*a*]pyrene collected from samples of suspected exposure routes, such as air and skin, and compared to the concentration of 1-hydroxypyrene at the end of the last shift of the work week (ACGIH, 2019). The adjusted BEI is considered the maximum acceptable urinary concentration of 1-hydroxypyrene for each worker, but due to the carcinogenicity of some PAHs, the ACGIH recommends exposures be kept as low as reasonably achievable (ACGIH, 2019).

The overall objective of this study was to develop a representative occupational exposure assessment of PAH exposure for RCTS workers based on work site surveys. This study is the first occupational exposure assessment for PAHs among refined coal tar sealant workers. The specific aims of this paper are: 1) to quantify full-shift airborne occupational exposures to PAHs for RCTS workers; 2) to assess dermal exposure to PAH among RCTS workers; 3) to quantify biomarkers of PAH exposure in workers' urine; 4) to identify specific job titles associated with RCTS work and evaluate how that affects exposure; 5) apply these results to a biological exposure index to assess risk of potential genotoxicity from occupational exposures.

2. Methods

2.1. Identifying companies and survey sites

This study focused on construction contracting companies with expertise in pavement sealing and evaluating job sites where pavement sealing with RCTS products was

performed. These companies employ crews that move to different job sites as the work is completed, causing varied exposure duration within shifts ranging from five to 10 h. RCTS product samples, personal and area air samples, skin wipe samples, and spot urine samples were collected for all survey sites. A total of 22 PAHs and seven urinary metabolites were quantified in various matrices and the corresponding abbreviations were defined. Table 1 focuses on PAHs with IARC classifications which indicate potential human carcinogenicity, and PAHs whose urinary metabolites where applied to statistical modelling in this manuscript. Supplemental Table S1 includes the remaining PAHs included in this assessment, that are not suspected or known carcinogens, and were not used for statistical modelling.

2.2. Participants

The study was approved by the NIOSH Institutional Review Board. Once a company agreed to participate, individual employees were voluntarily recruited prior to the first shift of the visit. Both men and women who work with RCTS were considered eligible for this study. The study was described to workers and an informed consent was reviewed and signed by participants.

2.3. Survey sites

Three companies participated in this study, referred to here as companies A, B and C. All sites were visited between the months of July and October 2016–18 and included sampling of workers over 1 to 4 workdays. During the four-day site visit at company A, a series of small hotel and motel parking lots were sealed, along with a few small residential driveways on the first day of sampling. There were four visits to company B. Each visit lasted several days, and crews surfaced a large industrial parking lot, two commercial parking lots, an airport, and commercial and residential parking lots and driveways. Some crew members at company B participated in sampling during multiple visits because the visits occurred at different times. At company C, a very large industrial parking lot was surfaced over 2 days.

The number of workers in crews at each site ranged from two to nine. These workers performed tasks such as: site preparation (cleaning and crack repair); preparation of RCTS equipment and supplies (including mixing the product and transferring it into the trucks); manual application of sealant to difficult areas (e.g., use of brushes or other tools where overspray is not wanted); application, including use of a hand-held spray-wand application of sealant to the general area, application using a driven sealer spray-squeegee machine (a truck-mounted spray-squeegee device), and assisting with general application (e.g. handling supply hoses, moving sealant tank, and driving sealant truck); cleanup; and general oversight of work. Although work tasks varied, workers were delineated as applicator or non-applicator. Applicators were more likely to perform tasks such as mixing, applying, and handling coal tar sealant directly. In contrast, non-applicators were tasked with preparatory work (e.g., cleaning surfaces prior to application) that did not require as much direct handling of the sealant product. However, they still worked the same number of hours and were close to the sealant for most of the workday.

2.4. RCTS product sampling of sealant material

One RCTS product sample of sealant material was collected for each batch of RCTS mixed, totaling eight RCTS product samples. Samples for each batch used or mixed during the field visit were collected in pre-cleaned 120 mL amber glass jars (Thermo Scientific Cat. No. 241–0120 Waltham, MA) directly from the RCTS tank. Samples were analyzed by the NIOSH contract laboratory using a modification of Environmental Protection Agency (EPA) Method 8270D (EPA, 2014). Briefly, 1 g of RCTS product material was weighed into a 40 mL volatile organic compound analysis (VOA) vial (Thermo Scientific I-Chem™ Cat. No. 05–719-118 Waltham, MA, USA) and extracted with 10 mL of methylene chloride. The samples were placed in an ultrasonic bath with ice for 20 min. The samples were shielded from light and allowed to settle over 48 h. Next, dilutions were prepared, and an internal standard (consisting of: naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12) was added to each vial, briefly mixed on a vortex, and PAHs were quantified using gas chromatography/mass spectroscopy (GC/MS).

2.5. Air sampling

Personal breathing zone (PBZ) and area air samples were collected by NIOSH staff at every location using a modification of NIOSH Manual of Analytical Methods (NMAM) 5515 (NIOSH, 1994). The important changes were the use of the OSHA Versatile Sampler (OVS-7 Cat. No. 226–57 SKC Inc. Eighty-Four PA) that combines the filter and sorbent in a single glass tube to collect both vapor and aerosol (Achutan et al., 2009; Eide et al., 2010) and analysis using gas chromatography-mass spectrometry in selected ion monitoring (GC-MS SIM) rather than gas chromatography-flame ionization detector (EPA, 2014). Method validation studies examined the method performance for all analytes (Table 1 and Supplemental Table S1) as described by chapter ME of the 5th edition, NMAM (NIOSH, 2016). Validation samples were spiked with a combination of all PAHs in Tables 1 and S1 with a concentration range of 0.5–20 μg/sample for each analyte (n = 6 replicates).Samples were measured over a range of 0.5–20 μg/sample (n = 6 for each analyte).The results of this sample set gave acceptable recoveries for all the compounds. The Limits of Detection (LOD) for all compounds were 0.05–0.08 μg/sample while the Limit of Quantitation (LOQ) was 0.17–0.26 μg/sample.

To collect PBZ samples, each participant wore a personal sampling train that included an OSHA Versatile Sampler connected by flexible tubing to a sample pump. Workplace air was drawn through the sampler using a personal sampling pump operating at 1 L/min (AirChek XR-5000 SKC Inc. Eighty-Four PA). Sample collection continued over the entire work shift for each worker. Sampling pumps were pre- and post-calibrated in-line with Dry Cal Defender 521 and 520 calibrators (Bios International, Butler Park, NJ, USA). Samples were stored under refrigeration until shipped to the NIOSH contract laboratory for analysis.

Area air samples were collected each day to measure PAHs in ambient air. Sampling trains and pumps were placed approximately 5–20 feet from the edges of work areas (area air samples). The number and orientation of area samples were determined based on the size and shape of each work site. Samplers were placed across from one another on each side of roadways.

Twenty field blanks were collected to account for contaminant loadings on the sampling media that may have resulted from accumulative field and laboratory activities. Field blanks were prepared by removing the sampler caps for 30 s and then resealing the samplers. The blanks were randomly selected from the same lot of OVS-7 sorbent tubes used at each visit and submitted to the laboratory for analysis.

PBZ and area samples were analyzed by the NIOSH contract laboratory. Briefly, the OVS-7 samples were desorbed into 2 mL of methylene chloride. The filter and front section were desorbed together, and the back section was desorbed separately with the middle foam plug. Sample desorbates were placed in an ultrasonic bath with ice for 30 min, removed, and placed at room temperature for a minimum of 30 min. An aliquot was processed and analyzed using GC-MS SIM (EPA, 2014).

2.6. Skin wipe sampling

Skin wipe samples were collected from the hands and neck at the beginning and end of each worker's shift. Hand wipe samples were collected using a previously described method (Cavallari et al., 2012; Fent et al., 2014; Fent et al., 2014). Briefly, 2 mL of corn oil (Mazola, ACH Food Companies Inc. Oakbrook Terrace, IL. USA) was added to the palm of one hand. After rubbing the hands together in a washing motion for 1 min, the worker wiped the oil from their hands using an absorbent polyester wipe (AlphaWipe® 9 × 9, ITW Texwipe™ Cat. No. TX 1009 Kernersville, NC, USA). After collection, the skin wipe sample was transferred to a black opaque 50 mL centrifuge tube (Argos Technologies, Cat. No. UX-06344–35 Vernon Hills, IL, USA) and refrigerated until shipping to the laboratory for analysis. Levels of PAHs were standardized by the surface area of both hands (1070 cm^2 for males and 890 cm^2 for females) based on mean dermal exposure factor data (EPA, 2011).

Neck wipe samples were collected in a similar way to hand samples. Wearing clean gloves for each wipe sample, NIOSH personnel applied 2 mL of corn oil directly to the center of an absorbent polyester wipe. The wipe was folded such that the portion containing corn oil was facing outward and the NIOSH researcher wiped the worker's neck from behind the right ear to the left ear, between the hairline and shirt collar. A minimum of two passes were made, folding the wipe to present a clean, oiled surface with each pass. After collection, the wipe was transferred to a black opaque 50 mL centrifuge tube and refrigerated until shipped to the laboratory for analysis.

Field blank wipe samples were prepared by NIOSH staff by donning clean gloves and applying 2 mL of corn oil directly to the center of an absorbent polyester wipe. The wipe was folded at least two times and the wipe was transferred to a black opaque 50 mL centrifuge tube and samples were refrigerated until shipped to the NIOSH contract lab for analysis.

Skin wipes were analyzed by a modification of EPA 8270D method. The wipe samples were desorbed into 70 mL of methylene chloride. The sample desorbate was placed in an ultrasonic bath with ice for 30 min and then placed at room temperature for a minimum of 30 min. An aliquot was processed and analyzed using GC-MS SIM.

2.7. Urine samples

Two urine spot samples (pre-shift and post-shift) were collected from participating workers each workday. Urine samples were labeled for identification, coded for confidentiality, tested for specific gravity using a refractometer, and aliquoted in the field as follows: a glass tube for the analysis of hydroxylated PAHs, a cryovial for the analysis of cotinine, and a polypropylene vial for the analysis of creatinine. Samples were kept on ice in the field, transferred to a −20 °C freezer at the end of each workday, and stored frozen until laboratory analysis. PAH biomarkers in urine were quantified using on-line solid phase extraction-high performance liquid chromatography-tandem mass spectrometry: 1- and 2-hydroxynaphthalene, 2- and 3-hydroxyfluorene, 1-hydroxyphenanthrene and 2,3-hydroxyphenanthrene (the sum of 2- and 3-hydroxyphenanthrene isomers that could not be chromatographically resolved), and 1-hydroxypyrene. The analytical method and the quality assurance/quality control procedures have been described in depth before (Wang et al., 2017).

The concentration of cotinine, a metabolite of nicotine, in the urine samples of the workers was used to determine a worker's exposure to nicotine in tobacco and other nicotine-containing products. Cotinine was measured in urine samples using the Diagnostic Products Corporation Immulite® 2000 analytical platform (Siemens Healthineers Malvin, PA). The Immulite 2000 cotinine assay is an Food and Drug Administration (FDA) waived assay that is capable of differentiating passive from active tobacco users (Rodriguez et al., 2010). Cotinine values of 200 ng/mL or greater were selected to classify workers as smokers (Kim, 2016). Creatinine in each urine sample was quantified with the Vitros Autoanalyzer (Ortho Clinical Diagnosis, Raritan, NH). Urinary creatinine was used to normalize the urinary PAH biomarker concentrations for urine dilution. .

2.8. Data analysis and statistical methods

In calculating the summary statistics, non-detectable air, hand wipe, and neck wipe concentrations were assigned values using the β-substitution method (Ganser and Hewett, 2010). Median, geometric mean (GM), and geometric standard deviation (GSD) are presented for air, hand wipe post-shift, neck wipe post-shift, and urine pre-shift and post-shift concentrations. Median differences of urine pre-shift and post-shift concentrations are also provided. These summary statistics were computed for concentrations of twelve PAHs in air, hand wipe, and neck wipe samples, and for concentrations of seven PAH metabolites in urine samples. A Tukey-Kramer test was used to compare the mean concentration between each pairwise combination of PAHs in air, hand wipe, and neck wipe samples. Additionally, univariate linear regression models of RCTS product were conducted to determine unadjusted associations between molecular weight of individual PAHs and 1) logarithmic PBZ air PAH concentration, and 2) assemblage of PAHs in products and hand wipe post-shift concentrations.

Differences of creatinine adjusted urinary pre-shift and post-shift concentrations for each metabolite and summation of relevant metabolites for phenanthrene, fluorene, and naphthalene were calculated. These metabolites were summed because they come from the same parent compound to create three additional biomarkers: Sum-hydroxynaphthalene,

Sum-hydroxyfluorene, and Sum-hydroxyphenanthrene. A marginal median regression model incorporating an exchangeable working correlation structure was used to account for the statistical correlation among repeated measurements from the same worker (Chen et al., 2021). The estimated correlation parameter of the exchangeable working structure represented a correlation coefficient between responses of any two samples from the same worker. The use of median regression was not only for log-normally exposure data, but for asymmetric logged exposure data. After adjusting for company, multivariable models with relevant PAH concentrations in PBZ air samples, and post-shift hand wipe and neck wipe samples as the dependent variables were conducted for testing the job title (applicator vs. non-applicator). Models adjusting for company were also carried out with urinary biomarker concentration difference as the dependent variable, in which covariates including corresponding PAH concentrations in PBZ air samples, and post-shift hand wipe and neck wipe samples, and job title (applicator versus non-applicator) were evaluated. Statistical tests were two-sided at the 0.05 significance level. All analyses were performed in R version 4.0.4 (R Core Team, 2021).

2.9. Biological exposure index (BEI)

The ACGIH considers urinary 1-hydoxypyrene a surrogate marker for carcinogenic PAHs (ACGIH, 2017). Presence of 1-hydroxypyrene was assessed by using the ACGIH adjusted BEI (ACGIH, 2017). The adjusted BEI requires calculation of the ratio of pyrene to benzo[*a*]pyrene present in suspected routes of exposure. Workers' post-shift 1-hydroxypyrene results from the final day of sampling were compared to the BEI adjusted for the particular ratio of pyrene to benzo[a]pyrene in thei air, and hand and neck wipe samples. Therefore, adjusted BEIs were calculated for 26 PBZ air, hand wipe post-shift, and neck wipe post-shift samples, then compared to individual post-shift, end of work week, 1-hydroxypyrene urine results to assess the BEI for each suspected exposure route. For example, if a participant's post-shift 1-hydroxypyrene results were higher than their adjusted BEI for the exposure route in question (PBZ, hand or neck wipe), this was an indication of chronic occupational exposure and risk of genotoxicity.

Smoking status does not effect BEI considerations. The ACGIH has determined that smoking is very unlikely to elevate urinary concentrations of urinary 1-hydroxypyrene high enough to exceed the benchmark concentration of 2.5 μg/L, which they consider evidence of occupational exposure and risk of genotoxicity (ACGIH, 2019).

3. Results

3.1. Demographics

Twenty-one RCTS workers from three companies consented to participate in this study. Their corresponding environmental and biological data were used in the analyses (Table 2). Most workers were male (95%), non-applicator (71%), and non-smoking (52%). Among the six applicators, five of them were smokers. Only one worker was female, non-applicator, and non-smoker. Note that, because of different biology, the results we provided in the manuscript were for male workers only.

3.2. RCTS product results

Eight RCTS product samples were collected for this study, one from company A, six from company B, and one from company C. The distributions of RCTS product values (μg/g) of 12 PAHs and their corresponding molecular weights (g/mole) are presented in Fig. 1. Overall, phenanthrene and pyrene had the highest concentrations. The third sealant products supplied by company A had higher PAH concentrations relative to the other two companies.

3.3. Air results

A total of 68 PBZ samples were collected from 20 workers and the median number of samples collected from each worker was two, ranging from two to eight. Eleven of 12 analytes were detected in more than 50% of PBZ air samples in all companies (Table 3; results of the remaining ten analytes not selected are in Supplemental Table S2). Airborne naphthalene level was at least two orders of magnitude below occupational exposure limits. The three PAHs listed as carcinogens by ACGIH (benz[*a*]anthracene, chrysene, and benzo[*a*]pyrene) were detected in 69, 75, and 69%, respectively, of the workers' PBZ air samples. Naphthalene had significantly higher GM concentrations (all p-values < 0.001) than the other PAHs. Applicators had higher phenanthrene, benz[a]anthracene, chrysene, and benzo[k]fluoranthene median concentrations in PBZ air samples than non-applicators (p-value < 0.05) (Table 4). Detailed summary PAH concentrations in PBZ air samples for applicators and non-applicators across all three companies are in Supplemental Table S3. Summary concentrations of area air samples are also provided (Supplemental Table S4). The PAH GM concentrations in area air samples were significantly lower than in PBZ air samples (all analytes with p-values < 0.001). Note that PAH concentrations of all field blank air samples were below the LOD. We also found that, through the use of GM- and mean-oriented data, logarithmic GM concentrations of PAHs in PBZ air significantly decreased with increasing mean molecular weights of the PAHs (p-value = 0.004). This result was consistent with the finding in Achten and Andersson (2015).

3.4. Hand and neck wipe results

A total of 38 hand and neck wipe samples were collected from 20 workers and the median number of samples collected from each worker was one, ranging from one to four. Hand wipe post-shift GM concentrations of phenanthrene and pyrene were significantly higher than those of the other PAHs for all companies combined (p-values < 0.05) but were not significantly different from one another (Table 3). Among neck wipe post-shift samples, phenanthrene and pyrene had the greatest median and GM concentrations (Table 3). Applicators were more likely to have higher hand wipe and neck wipe post-shift median concentrations of most PAHs than non-applicators (Table 4). Medians and GMs of PAH concentrations in neck wipe samples were much lower than those in hand wipe samples (results not shown). In addition, through the use of GM- and mean-oriented data, GM concentrations of PAHs in post-shift hand wipes increased with increasing mean compositions of PAHs in the products (p-value < 0.001) (Supplemental Fig. S1). Note that PAH concentrations of all field blank wipe samples were below the LOD.

3.5. Urine results

A total of 75 urinary samples were collected from 20 workers. The median number of samples collected from each worker was three, ranging from two to four. Differences in post- and pre-shift urinary PAH biomarker concentrations were generally greatest for company B (Table 5). Medain differences for urinary biomarkers, 2-hydroxyfluorene, 3-hydroxyfluorene, Sum-hydroxyfluorene, 1-hydroxyphenanthrene, Sum-hydroxyphenanthrene, and 1-hydroxypyrene were significantly higher for company B than company C, and median concentration differences of 1-hydroxynaphthalene and 1-hydroxypyrene were higher for company B than company A (p-values < 0.05) (Table 5). The concentrations of Sum-hydroxyfluorene and Sum-hydroxyphenanthrene were dominated by 2-hydroxyfluorene and 2,3-hydroxyphenanthrene, respectively. In addition to the results analyzing adjusted urinary samples, the summary results of unadjusted urinary biomarkers are presented in Supplemental Table S5.

Urine biomarker concentration differences (i.e., pre- and post-shift) were significantly and positively related to naphthalene, fluorene, and phenanthrene PBZ air concentrations (p-values < 0.001, 0.04 and < 0.001, respectively) (Table 6). Urine concentration differences were also significantly associated with increased neck wipe post-shift fluorene concentrations. Job title was not significantly related to concentration differences. Summary statistics of environmental and biological data including the female are provided in supplemenal tables (Tables S6 and S7).

3.6. Biological exposure index (BEI) results

The ACGIH BEIs were adjusted by calculating the ratios of pyrene to benzo[*a*]pyrene (Table 7 and Supplemental Table S8). Unadjusted urinary last-day post-shift 1-hydroxypyrene concentrations, ranging from 0.5 to 377 μg/L, exceeded the adjusted BEI in almost every case. Of 18 end-of-week urine 1-hydroxypyrene sample results that could be compared to airborne pyrene to benzo[*a*]pyrene ratios (applied as the adjusted BEI), 17 were above the adjusted BEIs. Workers' end-of-week urine 1-hydroxypyrene concentrations also exceeded the BEI when using hand wipe and neck wipe samples for calculation.

4. Discussion

4.1. Composition of RCTS products

The chemical composition of RCTS product samples from companies indicate which exposures to expect. We found little difference in overall composition of PAHs present in RCTS between companies and batches (Fig. 1 and Supplemental Fig. S1). Company A had the highest summed PAH levels among the three companies. The small differences observed between companies could relate to differences in the chemical composition of the crude coal tar starting product or variance between batches mixed on job sites. One batch may have contained more water or filler agents than another. Depending on the size of a project, it may also be necessary to re-mix or rehydrate a batch of RCTS, potentially further altering the final product. Despite these small differences, our results suggest that the composition was similar among all companies (Fig. 1). All analytes found in RCTS product samples were found in PBZ samples or post-shift hand wipe samples.

Asphalt is a product containing the most comparable PAH profile and application environment, with published research, that could be identified for comparison of this data. Results from previous RCTS and asphalt product sampling conducted by the IARC indicate that concentrations of 13 PAHs included in this manuscript are almost all at least one thousand times higher in RCTS than asphalt (IARC, 2013). For example, the IARC monograph reported that the benzo[*a*]pyrene concentration in asphalt product samples had a range of 0.22–1.8 μg/g, whereas the range of benzo[*a*]pyrene concentration present in coal-tar pitch samples without filler agents was 11,360 to 15,170 μg/g (IARC, 2013). The concentrations of benzo[*a*]pyrene in the RCTS sealants, after adding filler agents, in the present study were 2,436, 1,896, and 1817 μg/g for companies A, B, and C, respectively.

4.2. PBZ and area air samples

PBZ samples were included in this exposure assessment to help determine the primary exposure route that effects RCTS workers. Area air samples represent the environment immediately surrounding work areas and PBZ samples illustrate personal airborne occupational exposures. All nine PAHs classified by IARC as possible human carcinogen (Group 2B) to known human carcinogen (Group 1) were detected in PBZ samples at all companies, except for dibenzo[*a,h*]anthracene, which was not found in PBZ samples from company A (Table 3). In this exposure assessment, the GM concentration for workers exposed to benzo[*a*]pyrene was 0.05 μg/m^3. For context, the GESTIS International Limit Value database, which reports international occupational exposure limits by country, reports airborne concentration limits ranging from 0.07 to 2.0 μg/m^3 for an 8-h workday (IFA, 2021).

Workers in this study were exposed to atmospheric PAHs that are known or suspected carcinogens at levels at least an order of magnitude higher than published exposures of asphalt workers. McClean et al. (2012) reported GMs of airborne pyrene and naphthalene concentrations of 0.06 and 0.83 μg/m^3. In this exposure assessment, GMs for pyrene and naphthalene were 0.96 μg/m^3 and 55.81 μg/m^3, respectively.

Of the twelve PAHs considered potentially carcinogenic or used in our staticistal modelling, only seven were detected on area samples at work sites (Supplemental Table S4). PAH concentrations in area air samples that were detected were an order of magnitude lower than PAH concentrations found in the PBZ results (Supplemental Tables S2, S3, & S4), despite close proximity of area air sampling to the surfaces being treated. The comparison of the area air sample results to PBZ concentrations suggests the primary source of cumulative airborne exposure is occupationally derived.

4.3. Implications of skin wipe concentrations

Skin wipe samples were included in this exposure assessment to help determine the primary exposure route that effects RCTS workers. Mid-molecular weight PAHs phenanthrene, pyrene, and chrysene, in that order, were measured in the highest concentrations in post-shift hand wipes (Table 3). The lower molecular weight PAHs, such as naphthalene, quinoline, and acenaphthene, also were detected on hand wipes but at much lower concentrations, and at lower concentrations than most of the higher molecular weight PAHs (benz[*a*]anthracene

– benzo[*g,h,i*]perylene). This finding contrasts with that reported for asphalt workers, for whom lower molecular weight, more volatile PAHs contributed the most to skin exposure (McClean et al., 2012).

There are no occupational exposure limits for skin exposures to PAHs; however, all nine PAHs classified as possible human carcinogens (Group 2B) or known human carcinogens (Group 1) were detected in post-shift hand wipes. The post-shift hand wipe GM of pyrene for all companies and visits was 5.32 μg/cm^2 (Table 3). These results are considerably higher than levels reported in a previous study of asphalt workers, that reported GMs of post-shift hand wipe levels of pyrene to be 0.285 ng/cm^2 (Cavallari et al., 2012). Naphthalene, classified as possibly carcinogenic to humans (Group 2B) by the IARC, is commonly measured in asphalt worker exposure research. Cavallari et al. reported a range of 0.23–1.2 ng/cm^2 of naphthalene, with a detection rate too low to calculate the GM on participants' hands. The hand wipe results in this study for RCTS workers for all companies for naphthalene had a GM of 0.17 μg/cm^2.

Benzo[*a*]pyrene is the only PAH identified in refined coal tar that is classified as a known carcinogen (McClean et al., 2004). The post-shift hand wipe GM of benzo[*a*]pyrene in this study was 2.52 ± 7.36 μg/cm^2. Recent research found that benzo[*a*]pyrene is continually absorbed and metabolized by human skin over 48 h, meaning repeated occupational exposures throughout the workweek have a cumulative effect that likely increases risk of genotoxicity (Bourgart et al., 2018).

4.4. PAH biomarkers in urine

Urinary metabolites were assessed in this manuscript to support the corresponding exposure data. By pairing exposure data and urine results, we were able to identify the likely source of PAH exposure. For further context, RCTS workers' urinary PAH biomarkers are compared to those of the general population. Average urinary metabolite concentrations for the general population are reported by NHANES. NHANES data includes both occupationally and non-occupationally exposed people.

The metabolites of naphthalene (1- & 2-hydroxynaphthalene) can be used to indicate other airborne exposures to PAHs, due to their similar volatility. According to an NHANES survey conducted in 2013–2014, the unadjusted GM metabolite concentrations of 1-hydroxynaphthalene and 2-hydroxynaphthalene are 1.71 and 4.24 μg/L in the general population for people over the age of 20 (CDC, 2021). RCTS workers in the current study had unadjusted post-shift urinary GM concentrations of 43.26 and 55.18 μg/L for 1-hydroxynaphthalene and 2-hydroxynaphthalene, respectively (Supplemental Table S5), indicating substantially higher exposures to PAHs than the representative population sampled by NHANES.

The metabolite of pyrene (1-hydroxypyrene) can be used as a surrogate for skin exposures among higher molecular weight PAHs in RCTS. According to the 2013–2014 NHANES survey, the unadjusted GM metabolite concentration of 1-hydroxypyrene is 128 ng/L for people over the age of 20 (CDC, 2021). Pesch et al. reported medians of unadjusted post-shift urinary concentrations for non-smoking asphalt pavers of 419, and 793 ng/L for pavers

who smoked (Pesch et al., 2011). Urinary concentrations of RCTS workers in this study had a GM of over 39,000ng/L 1-hydroxypyrene for smokers and nonsmokers combined. The urinary 1-hydroxypyrene concentrations for RCTS workers in this study were approximately 49 times higher than concentrations reported for asphalt workers that smoked, and over 300 times higher than the population sampled by NHANES (Supplemental Table S5).

Urinary 1-hydroxypyrene concentrations, for all workers, was above the BEI recommended by ACGIH when the pyrene to benzo[*a*]pyrene ratio for skin wipe samples were used to adjust the the BEI (Table 7). When the BEI was adjusted using PBZ values of pyrene to benzo[*a*]pyrene ratio, urinary 1-hydroxypyrene exceeded the BEI in 89% of workers. In many cases, worker 1-hydroxypyrene levels were orders of magnitude above the BEI (Supplemental Table S8). The BEI results indicate that PAH exposures are occupationally derived and highlight the need to be reduce workplace exposures to minimize risk of genotoxicity for RCTS workers.

The relationships between urinary biomarkers and potential explanatory variables, including exposures and job title, were not statistically significant between non-applicators and applicators. This could be because both groups have long-term, daily exposures to RCTS. The urinary metabolite 1-hydroxypyrene did not have a significant correlation with explanatory variables, consistent with a much lower airborne concentration of pyrene relative to the three other volatile PAHs found in the highest concentrtions in PBZ samples (naphthalene, phenanthrene, and fluorene) (Table 3). There was no correlation between urinary biomarkers and PAHs in hand wipes, despite hand wipes having much higher levels of PAHs than neck wipes.

However, there was a correlation between urinary biomarkers and PAHs in neck wipes (Table 6). A significant correlation was only found for the sum of both urinary metabolites of fluorene (2- and 3-hydroxyfluorene). The difference between hand wipe and neck wipe associations with urinary biomarkers could be related to differences in PAH exposures at different locations on the body.

The hands are more transient than the neck. For example, the hands were likely washed or wiped at least once during the shift, and therefore produced more variable results than the neck, which may remain untouched for most of a work day. Hand wipe results could reflect cumulative exposures over a shift or reflect an acute exposure immediately before sampling occurred. Meanwhile, the neck represents potential cumulative exposures via vapor deposition and is a less transient part of the body. The neck also absorbs PAHs more quickly than hands, with relative absorption index values of 1.41 and 0.68, respectively (VanRooij et al., 1993), which likely contributed to the correlation between urinary biomarkers and PAH concentrations found on the neck wipe samples.

4.5. Job task and personal protective equipment

Applicators had significantly higher PBZ and post-shift hand wipe concentrations than non-applicators (Table 4). These results are likely related to differences in work-related tasks between the two subgroups. Applicators conducted work that always required direct

contact with RCTS such as mixing and application, while non-applicators were more likely to conduct ancillary tasks conducted further from the RCTS product.

There were statistical significances in phenanthrene median concentration levels between applicator status for all three sample types (Table 4). As a mid-molecular weight PAH, phenanthrene is more likely to be found in the air and on the skin, than more, or less volatile PAHs found in RCTS. Phenanthrene was identified as the most abundant PAH in samples of the starting product and was reported in much higher concentrations on PBZ and skin wipe samples than any other PAH, except airborne naphthalene. Due to the combination of its relative abundance in the starting product and the higher concentrations present on all sample media (Table 3), phenanthrene may be a suitable surrogate for cumulative PAH exposures in future RCTS worker exposure assessments.

Workers did not wear personal protective equipment (PPE) consistently. Many workers wore long pants and work boots, while others wore shorts and shoes. There was intermittent use of gloves, booties, dust masks, and splash-protective suits. No difference in PPE was observed between applicators and non-applicators, except that applicators wore gloves when conducting certain tasks, such as mixing. One applicator was observed in a full Tyvek suit and face covering when operating the boom sprayer/squeegee apparatus on the back of a truck. Some workers were observed wearing the same clothes every day, which likely contributed to chronic and take-home exposures. Although there is currently no research specific to RCTS safety controls, providing employees with PPE and developing company policies for guidance could reduce RCTS workers' risk of genotoxicity.

4.6. Limitations

As a result of the difficulty in finding companies to participate, the study had a low sample size and one company was visited multiple times. More detailed data on PPE, demographics, and post-shift cleaning practices (i.e., hand washing methods) could have provided additional insight. Analysis of additional metabolites that can't be assessed via urinalysis, such as 3-hydroxybenzo[*a*]pyrene and 6-hydroxychrysene, may have yielded useful information.

5. Conclusions

The exposure results from RCTS worker samples cannot be explained by proximal factors such as nearby restaurants or construction. Air and skin concentration levels were substantially higher for RCTS workers than previously published levels among asphalt workers for all PAHs. PAH profiles on skin wipes were more consistent with RCTS sealant product than air samples. Last day post-shift urinary concentrations of 1-hydroxypyrene greatly exceeded the ACGIH BEI benchmark of 2.5 μg/L in 25 of 26 samples, which suggests occupational exposure and risk of genotoxicity. When pyrene and benzo[*a*]pyrene were both detected, concentration ratios from personal exposure samples were used to calculate the adjusted BEI. Concentrations of 1-hydroxypyrene exceeded the adjusted BEIs for air, hand wipes, and neck wipes in most cases. These results indicate the need to increase safety controls and exposure mitigation for RCTS workers.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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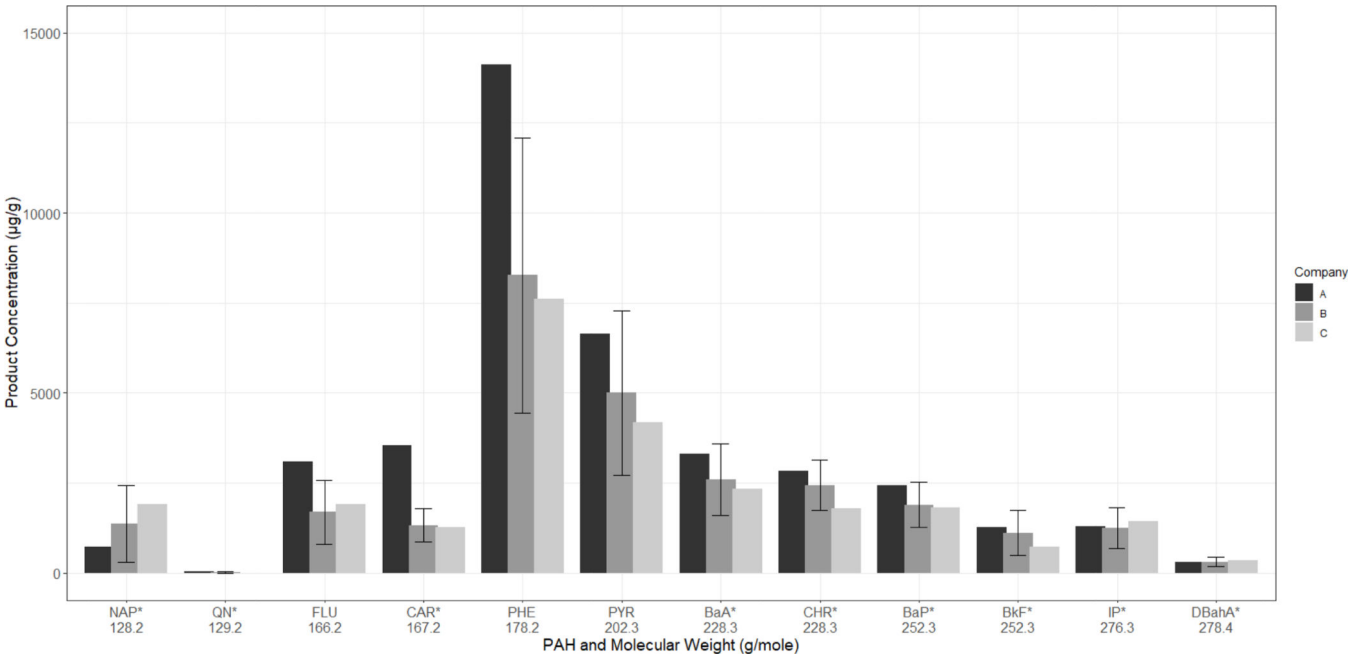

Figure 1.

RCTS product results (µg/g) by PAHs with corresponding molecular weights (g/mole) for three companies. Companies A and C had one RCTS product sample each. Company B had six samples, and values shown are arithmetic means with standard deviation. Asterisks were used to indicate the IARC Group 1 (carcinogenic to humans), Group 2A (probably carcinogenic to humans), and Group 2B (possibly carcinogenic to humans) PAHs.

Table 1.

PAHs quantified in air, hand wipe, and neck wipe samples, and PAH biomarkers in urine samples.

Analyte	IARC Classification*	CAS Number	Molecular Weight (g/mole)	Biomarker
PAH				
Naphthalene (NAP) [b]	2B	91-20-3	128.2	1-Hydroxynaphthalene (1-OHNAP), 2-Hydroxynaphthalene (2-OHNAP), and Sum-OHNAP
Fluorene (FLU) [b]	3	86-73-7	166.2	2-Hydroxyfluorene (2-OHFLU), 3-Hydroxyfluorene (3-OHFLU), and Sum-OHFLU
Phenanthrene (PHE) [b]	3	85-01-8	178.2	1-Hydroxyphenanthrene (1-OHPHE), 2,3-Hydroxyphenanthrene (2,3-OHPHE), and Sum-OHPHE
Pyrene (PYR) [b]	3	129-00-0	202.3	1-Hydroxypyrene (1-OHP)
Benz[*a*]anthracene (BaA)	2B	56-55-3	228.3	
Chrysene (CHR)	2B	218-01-9	228.3	
Benzo[*a*]pyrene (BaP)	1	50-32-8	252.3	
Benzo[*k*]fluoranthene (BkF)	2B	207-08-9	252.3	
Indeno[*1,2,3-cd*]pyrene (IP)	2B	193-39-5	276.3	
Dibenzo[*a,h*]anthracene (DBahA)	2A	53-70-3	278.4	
N-heterocyclic				
Quinoline (QN)	2B	91-22-5	129.2	
Carbazole (CAR)	2B	86-74-8	167.2	

Abbreviations are shown in parentheses.

[a] Group 1: Carcinogenic to humans; Group 2A: Probably carcinogenic to humans; Group 2B: Possibly carcinogenic to humans; Group 3: Not classifiable as to its carcinogenicity in humans (IARC, 2012). Refer to Supplemental Table S1 for abbreviations of PAHs that were not used for statistical modeling and not classifiable as carcinogenic,aor are currently considered not carcinogenic to humans, by the IARC.

[b] Analytes have corresponding urinary metabolites or biomarkers used for statistical modeling.

Table 2.

Characteristics of study participants or workers by company, N=21.

Company	A (N = 4)	B (N = 8)	C (N = 9)	Total (N=21)
Characteristic	**No. (%)**	**No. (%)**	**No. (%)**	**No. (%)**
Gender				
Male	3 (75)	8 (100)	9 (100)	20 (95)
Female	1 (25)	0	0	1 (5)
Age, years				
Mean ± SD	26 ± 6	41 ± 13	–	36 ± 13
Median	25	44	–	33
Range	21 – 33	25 – 54	–	21 – 54
Missing	1 (25)	2 (25)	9 (100)	12 (57)
Job Title				
Non-Applicator	3 (75)	5 (63)	7 (78)	15 (71)
Applicator	1 (25)	3 (38)	2 (22)	6 (29)
Smoking[a]				
No	3 (75)	4 (50)	4 (44)	11 (52)
Yes	1 (25)	4 (50)	5 (56)	10 (48)
Worked ≥ 20 days on coal tar sealant jobs during the prior 30 days				
No	4 (100)	1 (13)	–	5 (24)
Yes	0	7 (87)	–	7 (33)
Missing	0	0	9 (100)	9 (43)
Number of PBZ Air Samples	15	39	18	72
Number of Wipe Samples	4	25	9	38
Number of Urinary Samples	15	42	18	75

[a]Smoking is defined based on cotinine values of 200 ng/mL or greater.

Table 3.

PBZ air (μg/m^3), hand wipe post-shift (μg/cm^2), and neck wipe post-shift (μg/sample) concentrations of PAHs for all companies.

	PBZ Air Concentration (Number of Samples = 68)				Hand Wipe Post-Shift Concentration (Number of Samples = 37)				Neck Wipe Post-Shift Concentration (Number of Samples = 37)			
Analyte	**K < LOD* (%)**	**Medain†**	**GM†**	**GSD†**	**K < LOD* (%)**	**Medain†**	**GM†**	**GSD†**	**K < LOD* (%)**	**Medain†**	**GM†**	**GSD†**
NAP [e]	0 (0)	61.81	55.81	2.76	5 (14)	0.28	0.17	7.82	9 (24)	1.10	0.43	11.27
QN [e]	1 (1)	1.03	0.84	3.15	8 (22)	0.17	0.05	13.64	27 (73)	0.00	0.00	114.2
FLU	0 (0)	6.66	6.79	2.48	0 (0)	0.77	0.98	3.89	16 (43)	1.00	0.14	40.49
CAR [e]	4 (6)	0.36	0.29	3.61	1 (3)	1.31	1.44	6.62	23 (62)	0.00	0.02	64.45
PHE	0 (0)	11.26	10.09	2.34	0 (0)	6.07	7.96	3.76	1 (3)	5.60	6.22	6.05
PYR	0 (0)	0.98	0.96	2.89	1 (3)	5.79	5.32	9.41	11 (30)	3.00	1.00	30.55
BaA [e]	21 (31)	0.16	0.06	15.54	1 (3)	2.99	2.90	7.70	13 (35)	1.50	0.44	34.02
CHR [e]	17 (25)	0.20	0.10	11.19	1 (3)	3.55	3.50	7.86	13 (35)	1.60	0.53	35.35
BaP [c]	21 (31)	0.15	0.05	15.13	1 (3)	2.62	2.52	7.36	12 (33)	1.90	0.52	30.27
BkF [e]	29 (43)	0.07	0.01	35.90	1 (3)	1.40	1.32	6.14	19 (51)	0.00	0.08	54.12
IP [e]	24 (35)	0.11	0.03	20.92	1 (3)	1.87	1.78	6.43	14 (38)	1.30	0.28	35.74
DBahA [d]	54 (79)	0.00	0.00	533.7	1 (3)	0.46	0.48	4.54	27 (73)	0.00	0.00	82.36

[a] Non-detected values replaced using β-substitution (Ganser and Hewett, 2010). The PBZ air LOD for all analytes is 0.02 μg/m^3. Exposure levels of PAHs were standardized by the surface area of both hands based on mean dermal exposure factor data (1070 cm^2 for males (EPA, 2011)). The hand wipe LODs are 0.0009 μg/cm^2. The neck wipe LODs are 0.01 μg/sample.

[b] Reported medians, GMs, and GSDs for analytes with less than 50% detection rate may not be reliable.

[c] IARC Group 1: Carcinogenic to humans.

[d] IARC Group 2A: Probably carcinogenic to humans.

[e] IARC Group 2B: Possibly carcinogenic to humans.

Table 4.

Multivariable analysis using PBZ air (μg/m^3), hand wipe post-shift (μg/cm^2), and neck wipe post-shift concentrations (μg/sample) as the outcomes of interest (dependent variable) and comparing PAH concentrations of applicators with non-applicators (predictor)*, N of workers=20.

Dependent Variable	PBZ Air		Hand Wipe Post-Shift		Neck Wipe Post-Shift	
Analyte	**Difference** (SE)**	**P-Value**	**Difference** (SE)**	**P-Value**	**Difference** (SE)**	**P-Value**
NAP [e]	13.46 (10.86)	0.233	0.14 (0.07)	0.068	0.20 (0.15)	0.196
QN [e]	0.34 (0.33)	0.312	0.01 (0.03)	0.717	–	–
FLU	3.57 (1.79)	0.064	1.32 (0.13)	<0.001	1.70 (0.93)	0.086
CAR [e]	0.25 (0.18)	0.195	2.30 (0.12)	<0.001	1.40 (0.07)	<0.001
PHE	6.44 (2.42)	0.017	16.82 (0.50)	<0.001	8.90 (0.61)	<0.001
PYR	0.75 (0.75)	0.331	12.52 (0.15)	<0.001	7.20 (0.76)	<0.001
BaA [e]	0.10 (0.04)	0.021	5.33 (0.11)	<0.001	5.70 (0.50)	<0.001
CHR [e]	0.21 (0.04)	<0.001	8.04 (0.08)	<0.001	6.40 (0.42)	<0.001
BaP [c]	0.07 (0.11)	0.503	4.95 (0.38)	<0.001	4.00 (0.31)	<0.001
BkF [e]	0.06 (0.03)	0.043	1.59 (0.13)	<0.001	2.90 (0.15)	<0.001
IP [e]	0.08 (0.04)	0.081	2.15 (0.16)	<0.001	3.10 (0.44)	<0.001
DBahA [d]	–	–	0.97 (0.09)	<0.001	–	–

[a] Median regression models adjusting for company were used for the analyses. Models not convergent were marked as a dash.

[b] Difference of PAH median concentrations of applicators and non-applicators. Non-applicators were the reference group.

[c] IARC Group 1: Carcinogenic to humans.

[d] IARC Group 2A: Probably carcinogenic to humans.

[e] IARC Group 2B: Possibly carcinogenic to humans.

Table 5.

Urinary biomarker pre-shift and post-shift concentration (μg/g creatinine), and difference of pre- and post-shift concentrations by company.

	Pre-Shift			Post-Shift			Difference
	Median	**GM**	**GSD**	**Median**	**GM**	**GSD**	**Median**
All Companies (Number of Samples = 71)							
1-OHNAP	8.35	8.07	2.36	14.75	16.13	2.18	6.35
2-OHNAP	10.28	10.51	2.32	18.27	20.57	2.03	7.88
Sum-OHNAP	20.57	20.31	2.16	34.23	39.27	1.94	13.39
2-OHFLU	13.17	11.79	2.57	31.42	27.71	2.31	14.06
3-OHFLU	5.00	4.77	2.66	8.30	8.19	2.37	2.51
Sum-OHFLU	17.88	16.83	2.53	37.84	36.55	2.27	15.99
1-OHPHE	6.45	5.04	2.71	10.37	9.79	2.53	3.40
2,3-OHPHE	6.85	6.26	2.50	17.77	15.73	2.48	9.71
Sum-OHPHE	15.05	11.53	2.53	27.02	25.91	2.46	13.11
1-OHP	15.11	10.10	3.91	20.02	14.72	3.70	2.25
Company A[a] (Number of Samples = 11)							
1-OHNAP	6.25	7.01	1.66	8.90	11.29	1.53	3.90
2-OHNAP	6.06	7.88	2.09	13.13	13.78	1.66	4.90
2-OHFLU	8.83	9.34	2.42	30.29	23.80	2.31	14.37
3-OHFLU	3.59	3.51	2.68	5.98	5.84	2.42	2.04
1-OHPHE	4.10	3.58	2.98	8.76	6.38	2.87	2.41
2,3-OHPHE	4.53	4.34	2.87	16.02	11.04	2.94	4.77
1-OHP	9.60	4.41	6.88	13.42	5.27	6.66	0.08
Company B[a] (Number of Samples = 42)							
1-OHNAP	7.81	7.67	2.35	14.30	15.58	2.43	7.18
2-OHNAP	11.13	11.93	2.58	23.20	23.66	2.27	9.13
2-OHFLU	15.14	14.11	2.59	35.95	35.77	2.15	17.77
3-OHFLU	6.33	5.78	2.52	11.28	10.52	2.26	3.40
1-OHPHE	7.61	6.23	2.57	14.19	13.37	2.21	6.28
2,3-OHPHE	7.29	7.06	2.37	18.85	19.17	2.35	11.01
1-OHP	17.52	14.59	2.83	27.96	24.96	2.45	4.35
Company C[a] (Number of Samples = 18)							
1-OHNAP	9.58	9.89	2.81	21.95	21.73	1.77	9.41
2-OHNAP	10.05	9.33	1.77	18.21	18.97	1.46	8.24
2-OHFLU	7.46	8.93	2.49	13.58	16.76	2.20	6.36
3-OHFLU	3.59	3.67	2.85	4.87	5.62	2.19	1.42
1-OHPHE	3.48	3.78	2.68	6.85	6.15	2.43	1.86
2,3-OHPHE	6.65	5.91	2.56	13.14	12.32	2.33	5.24

	Pre-Shift			Post-Shift			Difference
	Median	**GM**	**GSD**	**Median**	**GM**	**GSD**	**Median**
1-OHP	8.44	7.11	4.05	8.36	8.04	3.04	0.66

Abbreviations of biomarkers: 1-Hydroxynaphthalene (1-OHNAP), 2-Hydroxynaphthalene (2-OHNAP), 2-Hydroxyfluorene (2-OHFLU), 3-Hydroxyfluorene (3-OHFLU), 1-Hydroxyphenanthrene (1-OHPHE), 2,3-Hydroxyphenanthrene (2,3-OHPHE), 1-Hydroxypyrene (1-OHP).

[a] 1 and 2 workers had 3 and 4 samples, respectively, in company A; 3, 8, and 3 workers had 2, 3, and 4 samples, respectively, in company B; 9 workers had 2 samples in company C.

Table 6.

Multivariable analysis using urine biomarker concentration difference between pre-shift and post-shift (μg/g creatinine) as the outcome of interest*, N or workers = 20.

		PBZ Air PAH		Hand Wipe Post-Shift		Neck Wipe Post-Shift	
Biomarker	**Analyte**	**Difference** (SE)**	**P-Value**	**Difference** (SE)**	**P-Value**	**Difference** (SE)**	**P-Value**
Sum-OHNAP	**NAP**	0.23 (0.05)	<0.001	7.46 (3.62)	0.056	4.85 (16.88)	0.777
Sum-OHFLU	**FLU**	1.87 (0.84)	0.040	0.16 (0.78)	0.839	0.95 (0.39)	0.028
Sum-OHPHE	**PHE**	1.00 (0.16)	<0.001	0.04 (0.04)	0.304	−0.04 (0.12)	0.737
1-OHP	**PYR**	1.70 (0.92)	0.082	0.03 (0.02)	0.261	0.01 (0.05)	0.803

[a]Median regression models adjusting for company were used for the analyses.

[b]Difference from median pre-shift to median post-shift values.

[c]IARC Group 2B: Possibly carcinogenic to humans.

Table 7.

Summary results of unadjusted urinary 1-OHP last-day post-shift concentrations (μg/L) and corresponding BEI values for 26 PBZ air, hand wipe post-shift, and neck wipe post-shift samples.

	N	BEI* Mean (PYR/BaP) (SD)	BEI Median (PYR/BaP) (Range)	N of 1-OHP > BEI* (%)
Air	18†	6.76 (4.61)	5.31 (2.43 – 17.62)	17 (94.4)
Hand Wipe	25†	2.19 (0.30)	2.20 (1.64 – 2.79)	25 (100)
Neck Wipe	21†	2.04 (1.11)	1.94 (0.68 – 6.20)	21 (100)
		Mean (μg/L) (SD)	**Median (μg/L) (Range)**	
Urinary 1-OHP	26‡	92.72 (94.22)	55.54 (0.53 – 377.0)	

*BEI: Biological exposure index; this index was calculated using ratio of PYR to BaP for each corresponding sample (ACGIH, 2019).

†BaP was not detected for eight air samples, one hand wipe sample, and four neck wipe samples. Also, PYR was not detected for one hand wipe sample and three neck wipe samples. Therefore, 18 air BEIs, 25 hand wipe BEIs, and 21 neck wipe BEIs were used to compare with the urinary 1-OHP data. Some workers were sampled for more than one week.